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13. ABSTRACT (Maximum 200 words) A new synthesis of high molecular weight polyaromatic quinonimines analogous to polyaniline was devised. Aromatic diamines condensed with substituted p-benzoquinones or anthraquinone in presence of titanium tetrachloride/Dabco to yield a new family of soluble, orange, film-forming polyaromatic quinonimines. Unlike polyaniline they were not electrically conductive. Polyaniline was alkylated by benzyl halides to form new soluble polyanilines. A cation-radical mechanism was established for the oxidative polymerization of aniline. Fundamental information on the polymerization of imine (>C=N) monomers was obtained.					
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**"Stereoregular Aromatic Polyquinonimines and Related Polymers as Electrically
Conductive, NLO-Active, Thermally Stable Polymers**

1. Description of the research problem studied, especially the scientific goals as they relate to the Army, and Scientific progress and accomplishments.

Polyaniline has established itself as an important electrically conducting organic polymer. Despite the simplicity of its preparation by oxidative polymerization, little was known about the polymerization mechanism or whether this black intractable material actually possessed a well-defined structure. Moreover, the inability to polymerize other anilines (other than o-methoxy aniline) to well-defined high-molecular weight, processable materials made it appropriate to look for other methods of synthesis. In particular, condensation polymerization suggested itself as an appropriate means to synthesize well-defined structures, particularly inasmuch as one can use model compounds to achieve very high yields and also to investigate their structures by X-ray and NMR methods.

Our research proceeded along two avenues, namely, the polyaromatic imines of benzoquinone and those of anthraquinone. We discovered a novel reagent for condensing these quinones with a wide variety of aromatic diamines, namely titanium tetrachloride-1,4-diazabicyclooctane (Dabco). In this way we were able to synthesize high molecular weight polyaromatic quinone imines from 2,5-dimethyl benzoquinone, 2,6-dimethyl benzoquinone, and 2, 3, 5, 6 tetramethyl benzoquinone. . However p-benzoquinone itself did not polymerize successfully. The polymers were high molecular weight, orange, film forming solids

Success was also achieved from anthraquinone and a wide variety of its substituted derivatives, using the above reagent with a wide variety of aromatic diamines. Again, these polymers were obtained in high yields and high molecular weights as orange film forming solids.

In contrast to black polyaniline, these well-defined polyaromatic quinone imines could not be rendered electrically conductive even by partial reduction to the emeraldine oxidation level. We are not clear yet as to why and the matter is still under investigation in collaboration with Professor Jean-Luc Bredas of this department.

On the view that "If you can't beat 'em, join 'em" we studied the chemistry of the oxidative polymerization of aniline. Through trapping experiments by appropriately selected additives, we were able to establish a cation radical chain mechanism for this oxidative polymerization. Although this had been discussed before, no definitive evidence had been provided. Our evidence excluded a possible nitrenium ion mechanism.

We also opened a way to a variety of novel derivatives of polyaniline by chemical modification of aniline. Replacing the N-hydrogens of polyaniline emeraldine base with sodium hydride in DMSO was carried out. If this polyanion was allowed to react with very reactive acylating or alkylating agents, a new series of polyaniline derivatives could

be made. A self-cross-linking reaction of polyaniline anion could be avoided by choice of very reactive alkylating agents such as benzyl or p-t-butylbenzylhalides. This approach to a wide variety of new polyaniline derivatives remains to be exploited.

Turning to the polymerization of monomers containing the C=N linkage, we continued our studies in this area. We showed that N-cyanomethane imine monomers gave modest molecular weight homopolymers and copolymers with radical or anionic initiators.

As to monomers containing electron-donating substituents on the imine nitrogen, we examined formaldehyde oxime and its alkyl derivatives. Low ceiling temperatures gave difficulties in this investigation, but we were able to carry out successful cationic copolymerizations.

These studies gave more fundamental information on the still incompletely understood problem of the polymerization of imine monomers.

2. **"Technology transfer" (any specific interactions or developments which would constitute technology transfer of the research results). Examples include patents, initiation of a start-up company based on research results, interactions with industry/Army R&D Laboratories or transfer of information which might impact the development of products.**

None

3. **"List of manuscripts" submitted or published under ARO sponsorship during this reporting period, including journal references.**

A - Condensation Routes to Polybenzoquinonimines

Y.Y. Chen and H.K. Hall, Jr., "Polycondensation of N-Chlorobenzoquinonimines" Polym. Bull. 20, 37 (1988).

Summary

Self-condensations of 4-chloroimino-2, 5-cyclohexadiene -1-one 1 (benzoquinone N-chloroimine), 2-tert-butyl-4-chloroimino -2, 5-cyclohexadiene -1-one 2, and 3-tert-butyl -4-chloroimino-2, 5-cyclohexadiene -1-one 3 in N-methylpyrrolidinone containing inorganic bases have been investigated. Monomer 1 gave polymers having inherent viscosities of 0.27-0.33 dLg⁻¹. Monomers 2 and 3 only gave oligomers. ¹H NMR spectra suggest that polymerization of 1 mainly occurs at C-2 and C-6 positions. A Michael-type addition mechanism, based on the high α -effect nucleophilicity of =NCl, is proposed.

H.W. Boone, J. Bryce, T. Lindgren, A.B. Padias and H.K. Hall, Jr., "Stereoregular Polybenzoquinone Imines from Methyl-substituted Benzoquinones", Macromolecules 30, 2797 (1997).

Abstract

The syntheses of model benzoquinone imines derived from 2, 5-dimethylbenzoquinone (25BQ), 2, 6-dimethylbenzoquinone (26BQ), and 2, 3, 5, 6-tetramethylbenzoquinone (DQ) are described. The stereochem. of the model compds. was investigated by x-ray crystal structure detn., UV spectroscopy and variable temp. NMR. These studies indicated that a polycondensation of methyl-substituted benzoquinone and arom. diamines would be feasible, and that a polymer incorporating 25BQ would preferentially exist in the anti configuration, while a polymer incorporating 26BQ or DQ would have no preference for either configuration. Polymns. were successfully carried out using both 4, 4'-thiodianiline and 4, 4'-methylenedianiline with 25BQ to yield moderately high mol. wt. material with Mw ranging from 13,000 to 30,000.

B - Condensation Routes to Polyanthraquinonimines

A. Everaerts, S. Roberts and H.K. Hall, Jr., "Synthesis and Properties of Semiconducting Aromatic Poly Quinonediiimines," J. Polymer Sci., Polym. Chem. Ed., 24, 1703 (1986).

Synopsis

A new class of poly-conjugated polymers has been obtained by condensation of anthraquinones with aromatic diamines in polyphosphoric acid. The polymers are black, intractable powders. Toward obtaining tractable materials, the effect of monomer structure on polymer tractability has been studied. Copolymerizations were also carried out to "soften" these materials. Electrical conductivities in the semiconducting range, 10^{-4} - 10^{-8} (ohm cm)⁻¹ were observed. Doping with iodine showed small increases.

P.A. Williams, K.A. Ellzey, A.B. Padias and H.K. Hall, Jr. "New Polyaromatic Quinoneimines from Anthraquinone" Macromolecules 26, 5820 (1993).

Abstract

A novel condensation polymn. to prep. fully conjugated poly (arylanthraquinoneimines) from anthraquinone and arom. diamines in the presence of TiCl₄ and Dabco is described. Sol., film-forming polymers with mol. wts. \leq 20,000 were prepd.

H.K. Hall, Jr., I. Yahagi, X. Drujon, P.A. Williams, M. Bruck and A.B. Padias, "Syntheses and Structures of Heterocyclic Quinone Imines as Model Compounds for Polyquinone Imines" Macromolecules 28, 9 (1995).

Abstract

The structures of model compounds for the polyaromatic quinone diimine polymers were determined. These polymers were obtained by

polycondensation of tricyclic quinones with aromatic diamines in the presence of titanium tetrachloride and 1, 4-diazabicyclo [2.2.2] octane. The *N*-phenyldiimine and monoimine derivatives of the following quinones were synthesized: naphthoquinone, 2-methyl- and 2-*tert*-butyloxazonaphthoquinone, 2, 2'-dimethylbis (oxazo) benzoquinone, and bithiophenobenzoquinone. X-ray single-crystal structure determinations are reported for the following derivatives: *N*, *N'*-bis (*p*-fluorophenyl) naphthoquinone 1, 4-diimine, *N*-phenyl 2-*tert*-butylnaphtho [2, 3-*d*] oxazole-4, 9-dione 4-imine and 9-imine, *N*-(*p*-fluorophenyl) -2-*tert*-butylnaphtho [2, 3-*d*] oxazole-9-one 4-imine, *N*-phenyl-2-isobutylnaphtho [2, 3-*d*] oxazole-9-one 4-imine, and *N*, *N'*-diphenylbenzo [1, 2-*b*: 4, 5-*b'*] dithiophene-4, 8-dione diimine. The following common features are observed for these structures: the central ring systems are planar in contrast to the anthraquinone diimine derivatives in which the central ring system is buckled, the *N*-phenyl ring is twisted out of the plane of the central ring system, and the *N*-phenyl rings are twisted toward the ring with the heteroatom and away from the C-H group on the adjacent ring. Molecular modeling calculations are found to be in agreement with the X-ray structures. The implications of the crystal structures of the model compounds for the polymeric structures are discussed.

P.A. Williams, J.M. Gosau, H.W. Boone, D.K. Park, A.B. Padias and H.K. Hall, Jr., "Novel Polyaromatic Quinone Imines" *Macromolecules* **28, 1 (1995).**

Abstract

A novel synthetic route to poly (quinone imines) has been developed. Reaction of anthraquinone (AQ) with aromatic diamines in the presence of titanium tetrachloride and 1, 4-diazabicyclo [2.2.2] octane (Dabco) as base in refluxing chloro- or *o*-dichlorobenzene led to high molecular weight polymers with the poly (quinone diimine) structure. Polymerization of AQ with methylene-4, 4'-dianiline resulted in a mixture of high molecular weight polymer (M_w 15 000) and oligomeric macrocycles. The polymerization of AQ was also accomplished with 4,4'-oxy- and 4, 4'-thiodianiline, as well as with *p*-phenylenediamine. The latter polymer is the dibenzo analog of the pernigraniline base form of polyaniline. *tert*-Butylantraquinone was also successfully used as a comonomer with the various aromatic diamines. All these polymers are red in color, soluble in organic solvents, and film-forming. Polymerizations of the aromatic diamines with heterocyclic-substituted benzoquinones, such as benzo [1, 2-*b*:4, 5-*b'*] dithiophene-4,8-dione, 2, 2'-dialkylbenzo [1,2-*d*: 5, 4-*d'*] dioxazole-4, 8-dione, and *N*, *N'*, 2, 2'-tetraalkylbenzo- [1, 2-*d*: 5, 4-*d'*] imidazole -4, 8-dione, were also investigated.

H.W. Boone, M.A. Bruck, R.B. Bates, A.B. Padias and H.K. Hall, Jr., "N,N'-Diphenyl-(1,4- and 1,5-dimethoxy)anthraquinone diimines: Butterfly Inversion of Anthraquinone Diimines", *J. Org. Chem.*, **60, 5279, (1995).**

Model compounds for polyaromatic quinone imines were synthesized and characterized by variable-temperature ^1H NMR spectroscopy and X-ray

single crystal structure determination. *N, N'*-Diphenyl-1, 4 (5)-dimethoxyanthraquinone 9, 10-diimines were synthesized by condensing 2 equiv of aniline with 1, 5-dimethoxyanthraquinone (**15DMAQ**) and 1, 4-dimethoxyanthraquinone (**14DMAQ**), respectively, in the presence of titanium tetrachloride and 1, 4-diazabicyclo [2.2.2] octane (**DABCO**). The X-ray single crystal structure determination of the diimine of **15DMAQ** is reported. The condensation of aniline with anthraquinones results in a buckling of the anthraquinone ring system, giving it a "butterfly" conformation while the diimine of **15DMAQ** has an anti configuration with the *N*-phenyl rings lying above the methoxy substituents. The diimine of **14DMAQ** has a syn configuration, again with these *N*-phenyl rings lying above the methoxy substituents. The symmetrical structural butterfly conformations of the diimines allowed for the observation of a dynamic butterfly inversion by variable-temperature ¹H NMR spectroscopy. The energy barriers for the butterfly inversion of *N*-phenyl **15DMAQ** and **14DMAQ** diimines are 9.5 kcal/mol. The implications of the crystal structure and molecular dynamics for the polymeric structures are discussed.

H.W. Boone and H.K. Hall, Jr., "Novel Polyaromatic Quinone Imines. 2. Synthesis of Model Compounds and Stereoregular Poly (Quinone Imines) from Disubstituted Anthraquinones", *Macromolecules* **29, 5835 (1996).**

Abstract

Novel poly (quinone diimines) from anthraquinones symmetrically disubstituted with solubilizing ethyleneoxy or long chain alkoxy groups have been synthesized and characterized. The disubstituted anthraquinones 1, 5-bis (2-methoxyethoxy) anthraquinone (**EO₁AQ**), 1, 5-bis (2-(2-methoxyethoxy) ethoxy) anthraquinone (**EP₂AQ**), 1, 5-bis (2-(2-methoxyethoxy) ethoxy) anthraquinone (**EO₂AQ**), 1, 5-bis (2-(2-methoxyethoxy) ethoxy) ethoxy) anthraquinone (**EO₃AQ**), 1, 5-bis (octyloxy) anthraquinone (**15OOAQ**), 2, 6-bis (octyloxy) anthraquinone (**26OOAQ**), and 1, 4-bis (octyloxy) anthraquinone (**14OOAQ**) were synthesized and condensed with aniline in the presence of titanium tetrachloride and 1, 4-diazabicyclo [2.2.2] octane to give *N, N'*-diphenyl -1, 5-bis (2-methoxyethoxy)_n anthraquinone 9, 10-diimine (**DEO_nAQ**, *n* = 1-3), *N, N'*-diphenyl-1, 5-bis (octyloxy) anthraquinone 9, 10-diimine (**15DOOAQ**), and *N, N'*-diphenyl-2, 6-bis (octyloxy)-anthraquinone 9, 10-diimine (**26DOOAQ**), respectively, as model compounds for the polymers. The relative stereochemistry of these diimines was determined by ¹H NMR spectroscopy. Polycondensation of the disubstituted anthraquinones with 4, 4'-thiodianiline (SDA) gave high molecular weight (*M_w* 30,000) poly-(anthraquinone diimines) and large macrocycles. Polycondensation of 1k 4-phenylenediamine (PDA) with **EO₂AQ** gave high molecular weight (*M_w* 14,000) polyaromatic anthraquinone diimines. PDA gave molecular weights of *M_w* 5000-23,000 for the bis (octyloxy)-substituted anthraquinones. The molecular weights of polymerizations incorporating PDA are lowered due to steric interactions of successive repeat units and solubility constraints.

C - Addition Polymerization of Imines and Azadienes

T. Kitayama, A.B. Padias, and H.K. Hall, Jr., "On the Polymerization of 1-substituted 2-Aza-1,3-butadienes," Polym. Bull., 17, 417 (1987).

Summary

Three 2-aza-1, 3-butadienes carrying substituents at the 1-position have been synthesized by flash vacuum pyrolysis of precursor cyclopentadiene cycloadducts. 1-Phenyl-2-aza-1, 3-butadiene led to low molecular weight polymer when exposed to anionic and radical initiators. 1-(2¹, 4¹, 4¹, 6¹-Trimethylphenyl)-2-aza-1, 3-butadiene and 1-*t*-butyl-2-aza-1, 3-butadiene were synthesized similarly, but they did not polymerize.

T. Kitayama and H.K. Hall, Jr., "Synthesis and Polymerization of 1-Azabutadiene Monomers," Macromolecules, 20, 1451 (1987).

Abstract

Four 1-aza-1, 3-butadiene monomers carrying substituents at the 1-aza position have been synthesized, and their abilities to polymerize have been assessed. The most successful monomers are *N*-phenyl-1-aza-1, 3-butadiene (1) and *N*-(2, 4, 6-trimethylphenyl)-1-aza-1, 3-butadiene (2). Their polymerization behavior was examined under acid, base, and free-radical conditions. Base-initiated polymerizations were the most successful. Monomer 2 gave vinyl polymer, whereas the polymer of 1 had both vinyl- and 4, 1-addition structures. Both of these monomers also polymerized with acidic initiators to yield polymers having both types of structural units. The various polymers were reduced with lithium borohydride to the corresponding saturated polyamines. Successful polymerizations of *N*-methoxy-1-aza-1, 3-butadiene (3) and *N*-(dimethylamino)-3-methyl-1-aza-1, 3-butadiene (4) were not achieved.

H.K. Hall, Jr., M. Ramezani and F.D. Saeva, "A New Azacyanocarbon, C₄N₄; Tricyanomethanimine," Tetrah. Lett. 29, 1235 (1988).

Abstract

2, 2-Dichloroethylene-1, 1-dicarbonitrile reacted with sodium azide to give 2, 2-diazidoethylene-1, 1-dicarbonitrile, which underwent thermolysis to give tricyanomethanimine, C₄N₄. The latter is as reactive as TCNE toward electron-rich molecules.

J.B. Kim and H.K. Hall, Jr., "Synthesis and Polymerization of 1-Carboethoxy-3-methyl-1-aza-1, 3-butadiene," Macromolecules 21, 1547 (1988).

Abstract

An azabutadiene with a highly electron-withdrawing group, carbethoxy, at the N-position was synthesized, and its polymerizability toward various initiators was investigated. *N*-Carbethoxy-3-methyl-1-aza-1, 3-butadiene

(CEMAB) gave highly pure 4, 1-addition polymer under anionic conditions and, with free radicals, gave polymers with mixed structures in low conversion. During the radical homopolymerization of CEMAB and copolymerization with electron-rich olefins, cycloaddition reactions involving carbon double bonds and imine linkage occurred to give inverse Diels-Alder type compounds. CEMAB is very sensitive to moisture and easily changed to a hydrate through addition of water to the imine double bond. The polymers were obtained as low-melting solids.

M. Ramezani, A.B. Padias, F.D. Saeva and H.K. Hall, Jr., "Synthesis and Reactions of Highly Electrophilic Imines Containing the N-Cyano Group." J. Org. Chem. 55, 1768 (1990).

Toluene solutions of tricyanomethanimine, 1, and methyl 3-aza-2, 3-dicyanoacrylate, 2, were synthesized by thermal decomposition of, respectively, 2, 2-diazido-1, 1-dicyanoethylene and methyl 3, 3-diazido-2-cyanoacrylate. Diethyl (cyanoimino) malonate, 3, was obtained from the reaction of diethyl ketomalonate with bis (trimethylsilyl) carbodiimide. None of these electrophilic imines could be isolated, because oligomerization occurred in every case. Dilute solutions of 1 and 2 in toluene were stable for several days, so the imines were characterized in solution. Cycloaddition reactions with 2, 3-dimethylbutadiene and cyclopentadiene lead to the expected Diels-Alder adducts. With *p*-methoxystyrene, spontaneous copolymerizations occurred with both 1 and 2. These imines were somewhat less electrophilic than tetracyanoethylene; they behave similarly in cycloaddition reactions, but in contrast they are also able to polymerize.

J.B. Kim, A.B. Padias and H.K. Hall, Jr., "Synthesis and Polymerization of New Azaethylene Monomers Carrying Electron-accepting Groups on Nitrogen," Macromolecules 23, 21 (1990).

Abstract

To explore the polymerizability of C=N monomers, the following compounds were synthesized: 2-phenylazaethylenecarbonitrile (benzylidenecyanamide; 1), 2-*tert*-butylazaethylenecarbonitrile (pivalidenecyanamide; 2), methyl 2-phenylazaethylenyl sulfone (*N*-(methylsulfonyl) benzylideneamine; 3), (ethyl 2-phenylazaethylenecarboxylate (*N*-carbethoxybenzylideneamine; 5). Their electrophilic character was appraised using hydrolysis rates and NMR data. Monomer 2 homopolymerized in high yield under both anionic and free-radical conditions to yield a low molecular weight polymer (DP=8). Monomer 2 polymerized poorly anionically and free radically. Monomer 4 oligomerized in low yield with weak bases. Compounds 3 and 5 did not polymerize. Low polymerizability of these compounds is ascribed to the required bulky substituent on carbon, and only the most electrophilic imine with a small cyano substituent on nitrogen and phenyl substituent on carbon is able to oligomerize effectively.

B.A. Bonner, A.B. Padias and H.K. Hall, Jr., "The Polymerization of 3-Methyl-N-(phenylsulfonyl)-1-aza-1,3-butadiene" Polym. Bull. 28, 517 (1992).

Summary

A study of the polymerizability of the first crystalline 1-azabutadiene carrying an electron-withdrawing group on nitrogen is described. A convenient one-step synthesis of 3-methyl-N-(phenylsulfonyl) -1-aza-1, 3-butadiene (MPAB) from methacrolein and benzenesulfonamide using titanium tetrachloride and triethylamine led to a crystalline azabutadiene monomer in good yield. With anionic initiators the monomer readily oligomerized to materials in which MPAB has reacted in a 4, 1-fashion. Under radical conditions the monomer did not homopolymerize, but did copolymerize with styrene monomers to polymers with molecular weights up to 10,000. These radical copolymerizations involved exclusive 4, 3-propagation (vinyl) for the azadiene monomer.

H.K. Hall, Jr. "Synthesis and Polymerization of Imines and Azadienes: New Polymerizable Monomers" Makromol. Chem., Macromol Symp. 54/55, 73 (1992).

Summary

1-Phenylsulfonylbicyclobutane (SBB) undergoes free radical homopolymerization to give soluble homopolymers, but attempted anionic homopolymerizations did not succeed. With free radical initiators, SBB copolymerizes with p-methoxystyrene, p-methylstyrene, methyl methacrylate, acrylonitrile and 1-cyanobicyclobutane to yield novel copolymers. The reactivity of SBB toward vinyl monomers is lower than that of 1-cyanobicyclobutane.

B. Roekens, A.B. Padias and H.K. Hall, Jr., "C,N-Dicyanomethanimine" J. Chem. Res. (S) 162 (1993).

Abstract

C, N-dicyanomethanimine was synthesized from β , β -diazidoacrylonitrile and trapped in soln. by cycloaddn. with cyclopentadiene.

D.D. Parker, A.B. Padias and H.K. Hall, Jr., "Synthesis and Polymerization Studies of N-Cyanomethanimine Monomers", J. Polym. Sci., Polym. Chem. Ed. 35, 2703 (1997).

Abstract

New imine monomers containing C-aryl and N-cyano substituents were synthesized and polymerized by both radical and anionic initiation. Homopolymerization yielded low molecular weight polymers ($M_n < 2100$): Higher yields were obtained with anionic initiation rather than radical initiation. Radical initiated copolymerization with p-methoxystyrene gave low yields of low molecular weight copolymers. Radical initiated copolymerization with methyl acrylate gave copolymers of 15,000-32,000

molecular weight in moderate yields, but with rather low incorporation of the imine monomer. The C-substituent affected the anionic and free radical reactivity similarly. © 1997 John Wiley & Sons, Inc. J Polymerization Sci A: Polymerization Chem 35: 2703-2710, 1997

Keywords: *N*-cyanomethanimine; homopolymerization; copolymerization; anionic; free radical.

D. D. Parker, A. B. Padias, and H. K. Hall, Jr., "Synthesis and Polymerization Studies of Formaldehyde Oxime and its Derivatives", In press. J. Polymer Sci.

Abstract

Formaldehyde oxime and three *O*-alkyl derivatives were examined as potential imine monomers. Formaldehyde oxime spontaneously polymerized below 60 °C, and did not polymerize above 60 °C (ceiling temperature), even in the presence of free radical or cationic initiators. The *O*-benzoyl derivative was isolated as the cyclic trimer, but could not be converted to the monomeric form. Formaldehyde *O*-benzyloxime was synthesized and isolated. Attempted homopolymerizations in the presence of free radical initiators only led to oligomers, while with cationic initiators only cyclic trimer was obtained. Copolymerizations with appropriate vinyl monomers using free radical and anionic initiators yielded only low molecular weight polymers, while cationic copolymerizations gave higher molecular weight and polymer yields. We conclude that the polymerizability of imines is extremely sensitive to the substitution pattern: imines with only a substituent on nitrogen are unstable and readily polymerize, while imines with more substituents generally do not polymerize. Electron-withdrawing substituents are more favorable to polymerizability.

D - Polyaniline

M.G. Mikhael, A.B. Padias and H.K. Hall, Jr., AN-Alkylation and N-Acylation of Polyaniline and Its Effect on Solubility and Electrical Conductivity@, J. Polym. Sci., Polym. Chem. Ed. 35, 1673 (1997)

Abstract

Various alkylating and acylating agents, with different electrophilicity, were allowed to react with polyaniline "emeraldine base" (Pan-EB) or its anion. Replacing the *N*-hydrogens of polyaniline by various acyl or benzyl groups strongly affected the solubility and the electrical conductivity of the polymer. Neutral Pan-EB was reacted with benzoyl chloride, *p*-*t*-butylbenzoyl chloride or pivaloyl chloride in *N, N'*-dimethylpropylene urea (DMPU) solutions. While the benzoyl and pivaloyl derivatives showed very poor solubility in common organic solvents, the *p*-*t*-butylbenzoyl derivative was readily soluble in THF, chloroform, DMAO, etc. As expected, these acyl derivatives showed diminished electrical conductivity relative to that of the parent Pan-EB. Benzyl chlorides did not react with neutral Pan-EB. Attempts to prepare solutions of the nitrogen anion of Pan-EB by reaction with sodium hydride in DMSO or DMPU let invariably to crosslinked

insoluble material. This was ascribed to Michael addition of the formed nitrogen anions to the quinonimine moieties. However forming the nitrogen anion in presence of *p*-*t*-butylbenzyl chloride trapped it to form *N*-benzylated Pan-EB. This was a soluble high molecular weight, electrically conductive ($4.3 \times 10^{-1} \text{ S cm}^{-1}$ as the hydrochloride) *N*-alkyl Pan-EB. Reacting Pan-EB with excess of both sodium hydride and benzyl chlorides led to film-forming per-benzylated Pan-leucoemeraldine reduced form. © 1997 John Wiley & Sons, Inc. J Polymerization Sci A: Polymerization Chem 35: 1673-1679, 1997

Keywords: polyaniline; acylation; alkylation; solubility; conductivity

Y. Ding, A.B. Padias and H. K. Hall, Jr., "Chemical Trapping Experiments Support a Cation-Radical Mechanism for the Oxidative Polymerization of Aniline", J. Polym. Sci., Polym. Chem. Ed. 37, 2569 (1999).

Abstract

The oxidative polymerization of aniline in aqueous acidic solution was carried out in the presence of a variety of organic compounds as potential traps for postulated intermediates. The polymerization was inhibited by hindered phenols and electron-rich alkenes, traps for cation-radicals. However, polyaniline was still obtained in the presence of electron-rich arenes, such as 1, 3-dimethoxybenzene and 1,4-dimethoxybenzene, known as excellent receptors of nitrenium ions. Polymerization of *N*-phenyl-1, 4-phenylenediamine was similarly carried out in the presence of potential traps. Polyaniline containing an *N*-phenyl group was obtained in the presence of 1, 3-dimethoxybenzene and 1, 4-dimethoxybenzene. Hindered phenols and 4-methoxystyrene only slightly inhibited polymerization of *N*-phenyl-1, 4-phenylenediamine which most probably proceeded by way of the stable diarylamino radical. Copolymerization of aniline with 10 wt% of *N*-phenyl-1, 4-phenylenediamine in the presence of these traps gave similar results to the polymerization of pure aniline. These results have led to the proposed cation-radical polymerization mechanism of aniline, in which the polymerization is a chain growth reaction through the combination of a polymeric cation-radical and an anilinium cation-radical. Step growth character is also present when a polymeric aminium cation-radical end combines with a diarylaminoended polymer. The copolymerization of *N*-phenyl-*p*-phenylenediamine can also occur by reaction of aniline cation-radical with a polyarylamine radical. The nitrenium mechanism was further rejected by the fact that attempted polymerization of *N*-phenylhydroxylamine, which forms authentic nitrenium ions in acid, failed to give polymer. © 1999 John Wiley & Sons, Inc. J Polymerization Sci A: Polymerization Chem 37: 2569-2579, 1999

Keywords: mechanism; polyaniline; cation-radical; nitrenium ion; trapping

E. - Other

Y.Y. Chen and H.K. Hall, Jr., "Polycondensation of Squaric Acid and *N*-Alkylcarbazoles," Polym. Bull., 16, 419 (1986).

Summary

1, 2-Dihydroxycyclobutene -3, 4-dione (squaric acid) was polycondensed with N-ethyl- and N- (1-butyl) carbazole in polyphosphoric acid to give polymers having 36-43% of 1, 2-oriented squarate units. The polymers are insoluble in organic solvents or sulfuric acid. Condensation of 1, 2-dichlorocyclobutene -3, 4-dione (squaryl dichloride) with N-1-butyl-carbazole in nitrobenzene gave 100% of 1, 2-oriented squarate units. This polymer is soluble in most organic solvents, and the molecular weight (M_w) is 1900 (DP = 6). The electrical conductivity was low, $<10^{-9}$ (ohm cm) $^{-1}$, and did not increase on treatment with iodine.

H.K. Hall, Jr., and D.W. Polis, "Starburst Polyarylamines and Their Semi-conducting Complexes as Potentially Electroactive Materials," Polym. Bull., 17, 409 (1987).

Summary

Highly branched "starburst" polyarylamines were synthesized by repetitive condensations of 2, 4-dinitrofluorobenzene with anilines, followed by reduction. These starburst arylamines were complexed with iodine to form semiconducting products. The reduced arylamines were examined by cyclic voltammetry.

H.K. Hall, Jr., T. Kuo, R.W. Lenz, and T.M. Leslie, "New Liquid Crystal Polyesters and Polyformals Containing Multiple p-Aryleneazo Groups: Liquid Crystal Polyazoaryl Sebacates," Macromolecules, 20, 2041 (1987).

Abstract

Multiazobisphenol monomers were synthesized. 4, 4'-(2-Methoxy-1, 4-phenylenebisazo) bisphenol, 4, 4'-(3, 3'-dimethyl-4, 4'-biphenylenebisazo) bisphenol (1) 4 and 4, 4'-[azobis (p-phenyleneazo)] bisphenol displayed liq. crystal (lc) properties, and model derivs. of 1 did likewise. Monomers and derivs. of 4-[(4-hydroxyphenyl)azo] -1-naphthol and 4, 4'-[oxybis-(p-phenyleneazo)] bisphenol showed no lc behavior. Thermotropic polyesters based on these multiazobisphenols were synthesized. Sebacate-contg. polyesters showed 1c behavior, while polymers based on isophthalic or 5-tert-butylisophthalic acid did not. Polyformals were also synthesized from these monomers, but none showed clear lc behavior.

T. Kuo and H.K. Hall, Jr., "Synthesis and Electrical Properties of Polyazoarylene Films," Synth. Metals, 22, 115 (1987).

Abstract

Polymers and copolymers containing p-azoarylene and p-azoxyarylene groups were synthesized by oxidative coupling of various aromatic diamines. Films were cast directly from the reaction mixtures or from the polymer solutions. The films were n-doped by sodium naphthalide or p-

doped by iodine. They showed electrical conductivities of 10^{-4} ohm cm^{-1} to 10^{-5} ohm $^{-1}$ cm^{-1} .

4. **“Scientific personnel” supported by this project and honors/awards/degrees received during this reporting period. Include awards and honors for yourself, even if not related to the ARO research.**

H.K. Hall, Jr.
Dallas Parker
James DiBattista
Brian Schmidt
Yong Ding
Michael Mikhael

5. **“Reports of inventions” (by title only)**

None